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# BIOLOGICAL ASSEMBLY OF HYBRID INORGANIC NANOMATERIALS (PREPRINT)

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The assembly of two or more inorganic nanoparticles results in hybrid materials with enhanced properties. These include improvements in catalytic activity, changes in optical behavior and potential gains in electronic properties. However, these are only attained through precise synthetic control of the resulting material with respect to structure, organization, size, and composition. Fortunately, biological systems are exceptional at the synthesis and assembly of diverse inorganic materials at many different length scales; and as result, has inspired many different approaches toward the biomimetic synthesis of hybrid inorganic materials.

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# Biological Assembly of Hybrid Inorganic Nanomaterials

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## ABSTRACT

The assembly of two or more inorganic nanoparticles results in hybrid materials with enhanced properties. These include improvements in catalytic activity, changes in optical behavior, and potential gains in electronic properties. However, these are only attained through precise synthetic control of the resulting material with respect to structure, organization, size, and composition. Fortunately, biological systems are exceptional at the synthesis and assembly of diverse inorganic materials at many different length scales; and as result, has inspired many different approaches towards the biomimetic synthesis of hybrid inorganic materials.

## KEYWORDS

Biological assembly, Inorganic hybrid materials, Quantum dot-gold, Co-encapsulation, Biosilification

## INTRODUCTION

The creation of new materials with enhanced optical, electronic, mechanical, and magnetic properties; in addition to high catalytic efficiencies, multi-functionality, and biomolecular recognition capability has become an emerging area of research and a goal of bionanotechnology. In nature, biological systems accomplish this proficiently by using various types of biomolecules to assemble a myriad of inorganic materials with superior properties and qualities. Examples include the mechanical robustness of

the glassy silica skeleton of marine sponges (*Euplectella sp.*) [1], magnetotactic behavior of iron oxide synthesized in bacteria [2], and 24-carat quality of biogenic gold by *Pedomicrobium*-Like bacteria [3,4].

Synthetically, these properties can be obtained by precisely integrating two or more different inorganic components in a defined geometry, spatial orientation, and structure, via a directing element or template which serves as the physical point of attachment. For example, gold and quantum dots show excellent optical properties individually such as strong plasmon resonances and intense luminescence; however, when assembled as an integrated structure, the hybrid structure develops fluorescence quenching or enhancement. Consequently, biomimetic approaches to hybrid inorganic materials have become increasingly attractive due to the abundance of biological motifs, engineered protein templates, effective biological interfaces, known receptor-ligand interactions, highly specific recognition processes, and the hybridization of DNA. For example, nanoparticles possessing complementary DNA strands have been assembled by hybridization to produce various gold nanoparticle structures; while combinations of different templates, interfaces, and recognition processes has been used to assemble unique inorganic heterostructures. In this review, we will describe the recent advances in the assembly of hybrid structures containing multiple inorganic components, methodologies, and associated properties, with an emphasis on the biological interface (Table 1).

## DNA ASSEMBLY

DNA mediated assembly represents the most widely utilized approach towards producing nanomaterials which has yielded structures of various dimensions, compositions, and properties. The first example of hybrid assembly involved the synthesis of a semi-conductor/metal structure consisting of a network of CdSe/ZnS quantum dots and gold nanoparticles functionalized with complimentary DNA strands [5]. More recently, these inorganic components were assembled into discrete structures with control as to the number of gold particles per quantum dot by the conjugation of only one oligonucleotide strand per gold particle as illustrated in the assembly scheme in Figure 1 through asymmetrical functionalization [6].

Assembled structures included a single gold particle associated with 1 quantum dot, 2 gold particles per quantum dot, 3 gold particles per quantum dot, and 4 gold particles around a central quantum dot (Figure 2). These were further separated into single populations of fixed structures using gel electrophoresis and the electrophoretic mobility of DNA. Similarly, Melvin and coworkers used DNA to assemble gold particles in close proximity to quantum dots that occupied 1+1 structures, and at close distances, fluorescence of the quantum dots was quenched by 85% [7]. Asymmetrical DNA functionalization has also been extended to the assembly of satellite gold structures obtained by the ligation of two smaller ssDNA chains, a non-functionalized extension chain and a chain functionalized to small gold particles, using a magnetic particle with DNA complementary to both smaller chains. After ligation and release of particles, gold nanoparticles displayed only the one ligated ssDNA [8].

DNA hybridization has also been exploited for the synthesis of $Au/SiO_2$ hybrid materials displaying intricate patterned structures. Mirkin *et al.* has shown the exquisite patterning of gold nanoparticles on the amorphous silica cell wall of diatoms (*Navicula* and *Syndedra*) seen in Figure 3 [9]. Diatoms represent excellent templates because of their silica exoskeleton, unique shape, architecture, high symmetry, micron scale length, species variability, and abundance in the ocean. As a result, they are easily cultured, processed (organic components digested by piranha), and modified with DNA. Accordingly, this presents a locally high concentration of DNA on the silica surface on exposed ridges, pores, and grooves of the diatom for the hybridization of complimentary DNA functionalized gold nanoparticles. After gold addition, characterization by SEM and TEM revealed a dense outer coating of 13 nm gold nanoparticles on the diatom *Navicula* surface. Because of the arrangement and ordering of these particles, they are applicable to nano optics, photonics, and catalysis.

Additional DNA mediated structures include a multi-target electrochemical probe and an assembled network of gold and protein encapsulated iron oxide particles [10,11]. In the former, a magnetic particle with three different 60-mer DNA targets to the BRCA1 breast-cancer gene was assembled using a sandwich hybridization approach with ZnS, CdS, and PbS quantum dot particles possessing non-complementary

ssDNA [10]. When hybridized, each orthogonal quantum dot particle provided a characteristic stripping voltammetric signal corresponding to a matched DNA target. Similarly, protein encapsulated iron oxide particles (ferritin) and gold nanoparticles were assembled via sandwich hybridization of a DNA modified protein shell of ferritin via streptavidin/biotin with non-complementary ssDNA resulting in a disordered network of closely associated gold nanoparticles and iron oxide ferritin cores. Aside from the hybridized DNA attachment, the use of ferritin as a supramolecular host for the mineralization of atypical substrates (CdS, $UO_2$, $Fe_2S_3$, MnO) within the empty protein cage is very appealing and provides a means to produce materials with magnetic, catalytic, and photoactive properties.

## STREPTAVIDIN/BIOTIN RECOGNITION

While DNA hybridization is extremely effective and remains the preferential choice for assembly; the use of non-DNA biological interfaces, motifs, and receptor-ligand interactions has made a substantial impact in the design of different assembled hybrid materials. Collectively, these include peptides, proteins, antibodies, and receptor-ligand pairs, with the most common being streptavidin/biotin. The affinity of streptavidin for biotin has been routinely employed for the association of two different targets such as linking DNA to a substrate, but also utilized to promote the assembly of quantum dot-gold nanohybrids. Kotov *et al.* used a quantum dot wire of CdTe coated with biotin as the organizational element to direct the binding of complementary streptavidin conjugated gold nanoparticles (Figure 1) [12]. Consequently, addition of gold particles (560 to 2250 gold particles per wire) to the quantum dot wire produced a strong increase in the photoluminescence intensity (PL) with 5 times enhancement upon binding. Enhancement is attributed to the interaction of plasmons in gold nanoparticles and excitons in quantum dots and marks the only reported example of substantial gains in luminescence. In contrast, streptavidin-biotin recognition of quantum dots and gold nanoparticles was utilized in an inhibition assay based on the modulation in FRET efficiency [13]. By contrast to PL enhancement of the gold/quantum dot wire structures, photoluminescence of the quantum dot conjugate was quenched by as much as 80% in the presence of matching gold biotin due to the geometry

of the quantum dot and the number of attached gold particles. The magnitude of quenching provided a benchmark for the measurement of avidin (biotin) concentration. Respectively, these structures illustrate the differing optical properties of quantum dots when assembled with metal nanoparticles, and provide a means for precisely tailoring optical properties via quenching or enhancement of fluorescence.

## PEPTIDE MEDIATED ASSEMBLY

Small synthetic peptides exemplify another type of biomolecular interface for hybrid assembly. Peptides provide variability, exhibit unique nanoparticle surface coordination unlike the simple conjugation of DNA or streptavidin through a thiol linkage, and present exposed binding sites imposed by the nanoparticle surface for antibody recognition or further derivatization. Also, they serve to impart biological activity or specific affinity on the nanoparticle surface. This activity was demonstrated by the antibody recognition of metal/semiconductor nanoparticles encapsulated by histidine-rich peptide epitopes to antibodies to the histidine-rich protein II from the malarial parasite [14].

Given the effectiveness of peptide epitope stabilized particles to elicit an antibody response, this recognition strategy was utilized for the assembly of inorganic heterostructures as highlighted in the following two examples and represented in Figure 1. In the first example, metal nanoparticles ($Cu^0$, $Pt^0$, $Ag^0$, and $Au^0$) stabilized by the tripeptide glutathione (γ-ECG) were assembled via a magnetic iron oxide particle conjugated with anti-rat IgG antibodies and then rat polyclonal antibodies specific to glutathione [15]. The $Fe_3O_4$-metal structures were separated by a magnetic field (neodymium magnet) and quantitated by energy dispersive X-ray spectroscopy [15]. By analogy, an alternate peptide epitope with the sequence of DYKDDDDK (Flag) was used for the antibody mediated construction of quantum dot/$Au^0$ hybrid structures. Briefly, gold particles were synthesized with the Flag peptide, while quantum dots were conjugated with biotinylated antibodies to the Flag epitope. Addition of both components resulted in the assembly of discrete Qdot/$Au^0$-peptide structures which consisted of 4 + 1, 2 + 1, and 1 + 1 assemblies by TEM analysis. Optically, these structures exhibited increased quenching of fluorescence dependent on the number of

attached gold particles and reached maximal quenching efficiency of 88 %. This behavior was also confirmed with theoretical calculations of exciton-energy transfer processes involving mixed numbers of gold particles per quantum dot [16,17].

This concept of quenching the quantum dot luminescence by assembling QD-gold structures has tremendous implications in medicine. West and co workers have developed quantum dots tethered to gold particles via a peptide interface which exhibited 70% quenching [18]. Unique to this structure is the peptide interface which features a specific sequence (GGLGPAGGCG) that is cleaved by the protease collagenase [18]. So consequently, in the presence of collagenase, the peptide tether of the QD-gold conjugate is readily cleaved rendering liberated quantum dots with recovered luminescence. In the near future, these hybrids are expected to provide a fluorescent beacon for the detection of protease activity associated with specific types of cancers and only become activated when that cancer is present.

Peptides designed with multi-functionality have expanded nanoparticle synthesis beyond single composition metal nanoparticles making it possible to controllably synthesize mixed compositions of inorganic nanoparticles in defined structures. Consequently, multi-functional peptides have been used for the synthesis of bimetallic Au-Pd nanostructures (**Figure 1**) [19]. Peptides were designed to include multiple binding domains selective for each metal nanoparticle; for example, the FlgA3 peptide (DYKDDDDKP**AYSSGAPPMPPF**) contained two domains, a domain for stabilizing palladium nanoparticles (A3) and a domain for synthesizing gold (Flg), respectively. As a result, Au nanoparticles were uniformly decorated with small palladium particles that were catalytically active for hydrogenation. Similarly, Banerjee et al. used a peptide functionalized gold nanoparticle to mineralize germania nanoshells around gold [20].

## CO-ENCAPSULATION VIA BIOSILIFICATION

Alternative strategies in the synthesis of hybrid inorganic materials have focused on biomineralization processes; and in particular, the controlled synthesis of silica by marine unicellular

diatoms under ambient conditions. As mentioned earlier, diatoms possess a highly ornate structure composed of an integrated network of silica nanoparticles; and therefore, is regarded as a premier example of biomineralization and extensively studied. Since it is known that silica formation by diatoms occurs by condensation of silicic acid by post-translationally modified peptides and proteins, peptide analogs have been used to mimic this biosilicification process. Biomimetically derived silica offers porosity, multiple sizes, and an excellent matrix for incorporation of other materials as first demonstrated by the entrapment of enzymes in silica spheres and later inorganic materials [21,22]. Encapsulation of materials occurs by introducing the inorganic particle along with the biomimetic template during silica condensation (Figure 1). Upon silica condensation, the inorganic particles become entrapped within the matrix. For encapsulated materials, the silica matrix serves to stabilize particles against aggregation, heat, and oxidizing conditions; thereby localizing particles within a confined and protective environment.

Silica entrapped inorganic materials have included CoPt [21], Au [22], CdSe/ZnS quantum dots [22], and magnetic iron oxide particles [21]; although, many more materials are suitable for encapsulation as well as the number of different particle types that can be co-encapsulated. Currently, both quantum dots and CoPt particles have been co-encapsulated within the silica matrix as demonstrated in figure 4 in by the TEM micrograph, but it is likely that more materials can be accommodated.

## CONCLUSIONS

The examples presented in this review illustrate the effectiveness of biological interfaces in assembling diverse materials via recognition events between a biological component and its counterpart with excellent efficiency. The collection of various biomolecules has afforded different structures, geometries, ratios of components, and combinations of inorganic materials which include silica with gold, quantum dots, iron oxide, or cobalt-platinum particles, and to a greater extent, quantum dot-gold materials which are otherwise unattainable by current synthetic strategies. The assembled materials were shown to exhibit interesting properties when assembled as best exemplified by the quenching of quantum dot fluorescence and

applied to the measurement of avidin concentration. The use of biological components for assembly ultimately provides a general platform which can be extended to many more materials and a large number of potentially viable biological templates/processes.

Figure 1. Bio-mediated assembly strategies.

Figure 2. TEM images of discrete QD-Au structures by DNA mediated assembly. Structures were separated by gel electrophoresis. (a) $QD(Au)_1$. (b) $QD(Au)_2$. (c) $QD(Au)_3$. (d) $QD(Au)_4$. Scale bar is 100 nm. Reprinted with permission from Fu, A.; Micheel, C. M.; Cha, J.; Chang, H.; Yang, H.; Alivasatos, A. P. *J. Am. Chem. Soc.* **2004**, *126*, 10832-10833. Copyright 2004 American Chemical Society.

Figure 3. SEM images of DNA-functionalized *Navicula* diatoms coated with complementary DNA-modified gold nanoparticles. Images are of a single frustule. Reprinted from Rosi, N.L.; Thaxton, C.S.; Mirkin, C.A. *Angew. Chem. Int. Ed.* **2004**, *43*, 5500-5503. Copyright 2004 Wiley-VCH Publishers.

Figure 4. TEM micrograph of CoPt nanoparticles entrapped in biomimetic silica. (Inset) HRTEM of the boxed region. Naik, R. R.; Tomczak, M. M.; Luckarift, H. R.; Spain, J. C.; Stone, M. O. *Chem. Commun.* **2004**, 1684-1685. Reproduced by permission of The Royal Society of Chemistry.

Table 1. Inorganic heterostructures assembled by various biomolecular building blocks.

| Hybrid | Biological building block | Structure | Properties | Ref. # |
|---|---|---|---|---|
| QD-$Au^0$ | DNA | "AB" structure | NA | 1 |
| QD-$Au^0$ | DNA | Discrete structures | NA | 6 |
| QD-$Au^0$ | DNA | 1:1 structure | Quenched fluor. | 7 |
| $Fe_3O_4$(ferritin)-$Au^0$ | DNA | aggregates | Shifted plasmon | 11 |
| $SiO_2$(diatom)-$Au^0$ | DNA | Patterned $Au^0$ | Shifted plasmon | 9 |
| CdTe-$Au^0$ | Strept/Biotin | $Au^0$ coated CdTe wire | Enhanced fluor. | 12 |
| QD-$Au^0$ | Strept/Biotin | $Au^0$ coated QD core | Quenched fluor. | 13 |
| QD-$Au^0$ | Antibody/epitope | Discrete structures | Quenched fluor. | 16 |
| QD-$Au^0$ | Peptide | NA | Quenched fluor | 18 |
| $Fe_3O_4$-$Ag^0$ | Antibody/epitope | NA | NA | 15 |
| Au-Pd | Peptide | Au decorated w/ Pd | Enhanced activity | 19 |
| Au-$GeO_2$ | Peptide | Au with $GeO_2$ shell | NA | 20 |
| QD-$SiO_2$ | R5 peptide | Encapsulated QD | QD fluor. | 22 |
| $Fe_3O_4$-$SiO_2$ | R5 peptide | Encapsulated $Fe_3O_4$ | Magnetic | 21 |
| CoPt-$SiO_2$ | R5 peptide | Encapsulated CoPt | NA | 21 |
| $Au^0$-$SiO_2$ | Dendrimer | Encapsulated $Au^0$ | NA | 22 |

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